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ENGINEERS

CHEMISTS

Plateau Engineering, Inc. 840 Rood Avenue Grand Junction, Colo. 81501 9-22-78

Attention: Mr. Edward Carpenter

Subject: Vanadium Queen Mine

Dear Mr. Carpenter:

Following is a summary of the results of our investigation into possible treatment processes for the mine drainage water from the Vanadium Queen Mine, and our recommendations.

A preliminary review of the applicable industry literature has revealed nothing new in the field with the exception of some recent developments in ion exchange technology (1)(2)(3)(4) related to concentration of dilute solutions for direct resource recovery by a second means (solvent extraction, precipitation, electrodeposition or other (5)). The Mine drainage in question does not economically fit any of the above processes because of low flow rates and low concentration of recoverable minerals. A review of the latest analytical literature failed, also, to provide anything better than existing technology. It is from the reports in this literature, of chemical separations of increased effeciency, that new commercial processes are derived. It is interesting to note, however, that barium carbonate and barium sulphate collection and concentration techniques are still the ones that are used the most

Our conclusion from the above exercise was that the barium chloride process was the best applicable technology, precipitated as the carbonate, sulphate or both, for the stream in question. Some of the highlights of the barium chloride process are as follows:

- The chemistry of the process is variable as most of the compounds removed are absorbed on the surface of the barium compound precipitates; a few are coprecipitated. The efficiency of the process depends on the chemistry of the water in question.
- 2). The barium chloride will precipitate efficiently as the carbonate from pH 7.0 on up, providing there are carbonate (CO_3) ions in the water and CO_2 is absent or low. The bicarbonate ion (HCO_3) is of no use if there are sulphate ions in the water (SO_4) , as the barium will precipitate as sulphate under these conditions.
- 3). At pH 7.0 to 8.9, the barium, precipated as the carbonate (8) will bring down trivalent iron (Fe⁺⁺⁺), aluminum (Al), titanium (Ti), zirconium (Zr), chromium (Cr) and uranium (U); also, in the presence of the preceding, phosphorus (P) and vanadium (V) will come down. Arsenic (As) and selenium (Se) are significantly reduced. The effect on radium at this pH is unknown.
- 4). The solubility of barium carbonate is very low, on the order of .0022 g/100ml in 70°F water at pH 7.0 and above. Its' solubility increases with lowering pH below 7.0. It is soluble in acids.
- 5). Radium is known to precipitate quantitatively on barium sulphate at about pH 4.2. It is not known what the removal efficiency is at other pH values. The sulphate precipate will form at any pH if there are sulphate ions available and is insoluble at all pH values (.0022 g/100ml @ 70°F), even in acids.

In its' simplest form, the process can be practiced by drip feeding the chemical solutions into the stream to be treated in a turbulent flow section of pipe or ditch leading to the settling pond. Turbulent flow can be ensured by placing overflow baffles in the bottom of the conduit. The chemical solutions can be made up by dissolving a measured amount of the dry chemical salts in some of the water to be treated, in a barrel. Since there are not enough carbonate or sulphate ions in the mine water in question, they would have to be added (as the sodium salts) along with the barium chloride. The barium chloride should be mixed and added separately.

Good mixing of the chemicals with the water to be treated is very important for good treating efficiency. The mixing section needs to be far enough ahead of the settling area that all mixing is complete before velocity is reduced. A second stage of mixing needs to be provided in a separate section at the head end of the settling pond. This is necessary because, while the treating efficiency is highest with the freshly precipitated barium, settling efficiency is very low. The particle diameter of the freshly precipitated barium carbonate or sulphate is about 0.1 microns and the settling rate without agglomeration would be in the range of 1cm/48hrs. Formation of the agglomerated precipitate can be speeded up by re-seeding the flow with some of the old precipitate in the second mixing stage. This can be accomplished with an air pipe anchored to the bottom, or other means. The average diameter of the agglomerate will be from 50 to 100 microns, depending on the effeciency of re-seeding. Settling rates should be in the range of 0.05 to 0.5 cm/second for the agglomerate.

The settling rates were confirmed by mixing/settling tests. Three 1000ml beakers were filled with tap water at pH 7.5. Sodium carbonate was added to the first beaker, sodium sulphate to the second, and a mixture to the third (amounts were the same as the maximum recommended treatment concentration given below). After the added chemicals were completely dissolved, a stoicheometric amount of 10% barium chloride solution was added and the resulting precipitate lightly mixed by hand stirring. All three beakers settled clear in 8 hours. The settled precipitate was then completely remixed and again allowed to settle. All three beakers settled clear in 21/2 hours this time. A third repeat produced a clear settling time of 1 hour. From this simple test it is easy to see the advantage of re-seeding with old precipitate.

One of the problems with the above process is that while some objectionable ions are removed from the water, soluble chloride ions are added:

$$BaCl_2 + Na_2CO_3 = Ba CO_3 + 2 NaCl$$

The usual limit of chloride ions in a discharge stream is 250 ppm. This limits the amount of barium chloride that can be added (the Utah limit is unknown, this point needs to be checked).

Another problem is that soluble barium compounds are poisonous. It is, therefore, essential that an excess of sulphate and/or carbonate ions be present to ensure that all of the barium is precipitated. This can be accomplished by adding a 10% excess of these ions, but this should be watched carefully as all of the excess adds to the total dissolved solids of the water. An excess can be tested for by adding a few drops of 10% barium chloride solution to a clear sample of treated water obtained from about half way down the settling pond. If a fine, white precipitate forms, there is an excess of carbonate or sulphate ions present.

The chemical usage for the above system, assuming an average flow rate of 2.5 GPM (an estimated reduction must be made to allow for evaporation in the pond) and a 250 ppm chloride concentration limit would be as follows: (includes the 10% excess of sulphate and/or carbonate ions).

	Chemi cal	Lbs/day
1).	Barium chloride Sodium sulphate	22.7 17.0
	or	
2).	Barium chloride Sodium carbonate	22.7 12.7
	or	
3).	Barium chloride Sodium sulphate Sodium carbonate	22.7 8.5 6.35

Chemical costs for the above cases would be as follows:

Case	\$/day	\$/year
1).	7.11	2595
2).	6.44	2351
3).	6.77	2473
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The above costs are based on a telephone quote from McKesson Chemical Co., Grand Junction, FOB Moab:

Barium chloride, technical grade, 100 lb. bags, ton lots. \$24.31/cwt \$ 7.26/cwt Sodium carbonate, technical grade, 100 lb. bags, ton lots. \$ 9.36/cwt Sodium sulphate, technical grade, 100 lb. bags, ton lots.

I thought it would be a good idea to talk to some of the Utah regulatory people regarding the proposed treatment to see what the official thinking on the increased chloride problem was. I was referred to a Mr. Steve McNiel with the Utah State Health Dept. In a telephone conversation with him, he recognized the problem in the trade-off between chlorides and the objectionable ions. He stated that it was a trade they were more than willing to make. The rest of the conversation related that radium was the most objectionable ion in question and any optimization should be aimed at its' removal. The Utah state regulations, especially as regards arsenic and selenium, are in a state of flux at the present time. Depending on the discharge source, rate, receiving stream use and dilution factors; the state is usually willing to negotiate on a case-by-case basis as to what will be allowed. There is a good chance that values above what has been previously stated would be allowed on all except radium. Mr. McNiel stated that they would make a ruling after reviewing the engineering report and test results of any proposed treatment plan. I made no mention of any specific property location in my conversation with him.

In light of the above, and the unknowns regarding the chemistry of the process with the water in question, I would recommend the following:

- Obtain a 10 gallon sample of the trypical water to be treated.
- Prepare 13, 1000ml as below and treat as indecated, at natural pH.
 - 1). Untreated
 - 2). 25% concentration treatment as the carbonate
 - 50%
 - 11 11 .. **
 - 4). 75% 5). 100%
 - 6). 25% concentration treatment as the sulphate
 - 7). 50% .. 11 11
 - 8). 11 75% .. 11 * ..
 - 11 9). 100% 11 11

10). 25% concentration treatment as mixed precipitate

11). 50% " " " " "

12). 75%

13). 100% " " " " "

The percentages given above are of the maximum recommend dosage. After the precipitate has settled, remix and let settle a second time.

- C). Filter the above treated samples and have tested for:
 - 1). Total disolved solids
 - 2). pH
 - 3) . Radium-226
 - 4) . Uranium
 - 5) . Dissolved arsenic
 - 6). Dissolved selenium
 - 7). Chlorides

The plotted data from the results of the above will allow the economics and efficiency to be determined.

- D). If none of the above are satisfactory, select the best one and duplicate the sample treatment to 3, 1000ml samples. Add 10, 30 and 50 ppm of ferric sulphate respectively to the 3 samples. Mix and settle as above and have tested as above.
- E). If none of the above are satisfactory, prepare one 1000ml sample of the 100% sulphate treatment, adjust to pH 4.2 with HCL and add the barium chloride. Mix and settle as above, filter, adjust to pH 7.0, re-treat sample with the best procedure as in"D" above, filter and test as above.

The above steps represent all of the alternatives that are open in the use of the barium chloride process and the best results, acceptable or not, will be determined accordingly. This is the type of information that the State will require before approving or negotiating a plan.

If I can be of any further help in the above matter, please call.

Yours very truly, Technolgy Management, Inc.

Carlon C. Chambers. P.E.

President

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